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equal to the amount of polymeric lithium reagent. By analysis of other reaction products such as 1-bromobutane, adsorbed alkyllithium reagent can be distinguished from polymeric lithium reagent. Synthetic procedures leading to polymeric alkali metal aromatic radical anions are also described. Synthetic applications of these polymeric alkali metal aromatic radical anions are also detailed. Reducations of transition metal complexes and alkyl halides by these polymeric radical anions parallel known chemistry of sodium naphthalene. \(\pi\)-Cyclopentadienyldicarbonyliron dimer is reduced to cyclopentadienyldicarbonyliron anion which in turn was trapped by chloromethylated polystyrene. Alkyl halides are either reduced to hydrocarbon products or else alkylate the organometallic polymer.

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Organic Coatings and Plastics Chemistry

Preparation and Characterization of Alkali Metal Organometallic Polymers

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PREPARATION AND CHARACTERIZATION OF ALKALI METAL ORGANOMETALLIC POLYMERS. D. E. Bergbreiter and J. M. Killough. Texas A&M University Department of Chemistry, College Station, Texas 77843.

Lithiated cross-linked insoluble polystyrene polymers have been prepared by several different procedures. In the case of organometallic polymers containing σ-bonded organolithium reagents, chromatographic procedures have been developed which can accurately quantitate the amount of organolithium species present. This analytical procedure employs the reaction of 1,2-dibromodecane with polystyryllithium which generates an amount of 1-decene equal to the amount of polymeric lithium reagent. By analysis of other reaction products such as 1-bromobutane, adsorbed alkyllithium reagent can be distinguished from polymeric lithium reagent. Synthetic procedures leading to polymeric alkali metal aromatic radical anions are also described. Synthetic applications of these polymeric alkali metal aromatic radical anions are also detailed. Reductions of transition metal complexes and alkyl halides by these polymeric radical anions parallel known chemistry of sodium naphthalene.  $\pi$ -Cyclopentadienyldicarbonyliron dimer is reduced to cyclopentadienyldicarbonyliron anion which in turn was trapped by chloromethylated polystyrene. Alkyl halides are either reduced to hydrocarbon products or else alkylate the organometallic polymer.

# Preparation and Characterization of Alkali Metal Organometallic Polymers

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Organometallic polymers have become particularly interesting in recent years because of their potential as catalysts, as functionalized polymer intermediates, and as synthetic reagents. Organometallic polymers containing carbon-metal bonds are of interest to the general areas of polymer supported catalysts, polymer chemistry, and synthesis and are the subject of this paper. In the work discussed below, we have been especially interested in the preparation and characterization of reactive alkali metal organometallic polymers which can be used in the synthesis of other functionalized polymers.

Our work in this area has dealt with organometallic derivatives of both organic and inorganic polymers. The initial studies which we carried out and which have now been published dealt primarily with derivatives of graphite and more specifically with potassium-graphite  $(C_8K)$ . In more recent work, we have concentrated on studies of organic polymers emphasizing lithiated polystyrenes as representative examples of reactive alkali metal organometallic polymers. The results of these studies described here include reasonably general analytical procedures for quantitating polystyryllithium and for differentiating polystyryllithium and for differentiating polystyryllithium from adsorbed lithium alkyls and alkoxides. Separate studies also described here include synthetic routes to novel polymer bound alkali metal aromatic radical anions and a preliminary account of the chemistry of these polymeric radical anions.

Results and Discussion

Polystyryllithium can be prepared in several different ways according to procedures previously described in the literature (e.g. equations 1-3). Following these procedures, we have prepared polystyryllithium from various types of divi-

nylbenzene crosslinked polystyrene polymers. Analysis of the resulting insoluble polymeric lithium reagents was carried out using the analytical procedure described below.

The analytical procedure we have developed for reactive alkali metal organometallic polymers is based on the well known reaction of soluble organolithium reagents with 1,2-dibromoethane to give ethylene and an alkyl bromide (equation 4).6 We reasoned that the reaction of insoluble crosslinked polystyryl-

lithium with 1,2-dibromodecane should parallel this known solution chemistry. Gas chromatographic analysis of the decene product from the reaction of excess 1,2-dibromodecane and metalated polymer could thus be used to determine the amount of polymeric lithium reagent present. An advantage of this procedure is that it can in principle distinguish between polymeric organometallic species and species that are merely adsorbed on the polymer. For example, polystyryllithium is often prepared by procedures which employ an excess of a soluble alkyllithium reagent such as n-butyllithium. In such cases, the resulting lithiated polystyrene could exist as a monomeric phenyllithium like species, as an intra-polymerically aggregated lithium reagent, as an aggregate with  $\underline{n}$ -butyllithium, or as some combination of these possible forms. In any case, comparison of the glpc results for 1-bromobutane and 1-decene formation after a 1,2-dibromodecane quench would permit us to distinguish between polystyryllithium and n-butyllithium since polymeric lithium reagent would generate only 1-decene while n-butyllithium would produce an equivalent of 1-bromobutane and 1-decene. The results of our studies using this type of analytical procedure are described in Table I and discussed in detail below.

As can be seen from the data in Table I, the analytical procedure described by equation 5 is applicable to a variety of different types of polystyryllithium reagents and allows us

to quantify even small amounts of polymeric lithium reagent. Since this procedure involves a reaction of an organolithium species rather than an acid-base titration, it distinguishes between organolithium reagents and other basic species such as lithium alkoxides. It has advantages over carboxylation folfowed by titrimetric analysis of the resulting polymeric carboxylic acid both in terms of sensitivity and in terms of convenience. The bromine incorporation into polystyrene expected according to the stoichiometry of equation 5 has been verified in several examples by ESCA spectroscopy although bromine incorporation was not quantitatively determined.

Table I. Reaction Products from the Reaction of 1,2-Dibromodecane with Insoluble Polymeric Lithium Reagents in Ethereal Solution at -78°C.

Polymer	Metalation Procedure (hours)	1-Decene (mmol per g polymer)	1-Bromobut (mmol per polymer)	
PS-H	A(1)	2.30	2.14	0.16
PS-H	A(8)	1.98	1.00	0.98
PS-H	A(20)	1.46	0.16	1.30
PS-H	$A(36)^3$	0.69	0.00.	0.69
PS-Br	B(4)	1.65	0.244	1.41_
PS-Br	B(20)	1.33	1.004	>0.335
PS-Br	B(12) <sup>3</sup>	0.70	0.00	0.70

\*\*Macroreticular polystyrene was used in all examples shown and either contained no functional groups other than hydrogen (PS-H), bromine at a level of 4.3 mmol/g (PS-Br), or mercuric chloride at a level of 2.8 mmol/g (PS-HgCl). 

\*\*Metalation procedures are described in reference 3 (A), 4 (B), and 5 (C). All metalations employed n-butyllithium as the alkyllithium reagent. Variations in the reaction time lead to different amounts of lithiated polymer (see text). 

\*\*The lithiated polymer was first washed with solvent to remove soluble and/or adsorbed base. 

\*\*4Octane formed from reaction of n-butyllithium and 1-bromobutane was a by-product in this reaction and is inculded in the this value. 

\*\*Since no correction was made in this datum for 1-bromobutane (and octane) formed during the metalation procedure this value for lithiated polymer is a minimum value.

A disadvantage of our procedure is that it is a batch process and either requires that a portion of insoluble lithiated polymer or an entire run be quenched. This procedure also gives only a lower limit for the amount of metalated sites as determined by the difference between the amount of 1-decene and 1-bromobutane in Table I since unforeseen side reactions cannot be completely excluded.

An interesting aspect of the studies described in Table I are those experiments in which excess n-butyllithium was Determination of the relative amounts of 1-decene and 1-bromobutane in quenches of these reactions permits us to distinguish between non-polymeric and polymeric organolithium species. Using this procedure we were then able to show that polystyryllithium prepared from brominated polystyrene can be washed completely free of soluble lithium reagent with 4-6 10-ml pentane washes. Typically these washes were continued until no soluble base could be detected in the wash solution. At this point a 1,2-dibromodecane quench showed up to 1-2 mmol of lithium reagent still present per g of polymer without any detectable amount of adsorbed n-buty1lithium. The resulting polystyryllithium in such a case presumable exists as a monomeric or more likely as an intrapolymerically aggregated lithium reagent. While we cannot unambiguously distinguish between these alternatives, experiments in which addition of n-butyllithium to thoroughly washed polystyryllithium led to adsorption of lithium reagent suggest that aggregation of polymeric lithium reagents can occur.

the absence of adsorbed n-butyllithium, aggregation could occur through site-site interactions which are now well precedented in other functionalized cross-linked polystyrenes:

The amount of time used in metalation procedures leading to lithiated polystyrenes was shown to be important in maximizing the amount of polymeric lithium reagent. For the reactions shown in equations 1-3, 8-24 hours was usually the most satisfactory amount of time for reaction. Longer times typically led to decreases in the amount of polymeric lithium reagent through unknown processes and shorter times often resulted in incomplete metalation. Optimal reaction times also may vary for other types of polymers.

In addition to working with  $\sigma$ -bonded organolithium poly-smers, we have also developed procedures leading to polymeric alkali metal aromatic radical anions. A functionalized polymeric precursor to a polymeric aromatic radical anion can be readily prepared by addition of an ethereal solution of anthrone to lithiated macroreticular polystyrene. Subsequent treatment of the polymer bound tertiary alcohol with paratoluenesulfonic acid in hot toluene yielded a polystyryl anthracene (equation 6). Reduction of this polymeric poly-

$$PSLi \cdot O \longrightarrow PS \longrightarrow H' \longrightarrow PS \longrightarrow (6)$$

cyclic aromatic compound with a tetrahydrofuran (THF) solution of sodium naphthalene according to equation 7 yields the polymeric radical anion. Formation of this metalated polystyrene radical anion is accompanied by rapid decolorization of the

THF solution of sodium naphthalene and concomitant development of a greenish color on the polymer. Gas chromatographic analysis of the clear supernatent liquid over this colored insoluble polymer showed that all the original naphthalene is present in solution. An aqueous quench of this solution also shows no soluble base indicating that the electron transfer reaction is complete. Complete electron transfer is not unexpected in view of the differences in reduction potentials of naphthalene and the polymeric polycyclic aromatic compound.

Preliminary experiments have shown that polymeric alkali metal aromatic radical anions like the one prepared in equation 7 can be synthetically useful and mechanistically interesting. For example, aromatic radical anions are known to be useful reducing agents for generation of anionic transition metal complexes. 9 Using the polymeric radical anion prepared as in equation 7 and π-cyclopentadienyldicarbonyliron dimer we were able to generate a nucleophilic iron complex which was trapped with 2% divinylbenzene crosslinked chloromethylated polystyrene. The resulting polymeric organoiron compound could be characterized by ir and by the characteristic rust color of the polymer. Aromatic radical anions are also known to be reactive reducing agents toward organic halides. 10 The polymeric alkali metal aromatic radical anions we have prepared undergo qualitatively similar reactions. Alkyl iodides, bromides, and chlorides are partially reduced to hydrocarbons and in some cases ir evidence shows that alkylation of the polymeric aromatic radical anions has occurred as well.

Acknowledgement. We thank the Office of Naval Research and the Texas A&M Center for Energy and Mineral Resources for support of this work.

### Experimental

General Methods. All reactions of air and water sensitive materials were carried out under argon or nitrogen atmospheres using standard techniques.11 Nitrogen was purified by passage through a drying tower of calcium chloride, argon was used without further purification. Tetrahydrofuran and other ethereal and hydrocarbon solvents were distilled from a purple suspension or solution of disodium benzophenone dianion prior to use. IR spectra were recorded as potassium bromide mulls on a Beckman 4260 spectrophotometer. ESCA spectra were recorded on a Hewlett-Packard 5950A spectrometer. Perkin-Elmer Model 3920 and Hewlett-Packard 5930A gas chromatographs were used for glpc analyses. Analyses were carried out on 6'x1/8" OV-17 columns at  $70^\circ$  using unexceptional internal standard techniques. All organic chemicals were purchased from the Aldrich Chemical Co. or other commercial sources and used as supplied. Inorganic chemicals were purchased from Alfa Inorganics, Strem Chemical Co., or Fischer Scientific Co. and used as supplied except for n-cyclopentadienylirondicarbonyl dimer which was recrystallized prior to use from acetone and water. Lithium reagents were purchased from the Aldrich Chemical Co. and analyzed prior to use by the method of Watson and Eastham. 12 Macroreticular polystyrene beads and brominated macroreticular polystyrene beads containing 4.36 or 4.1 mmol Br/g were purchased from the Aldrich Chemical Co., extracted with THF and dried prior to use. Merrifield resin containing 1.09 mequiv C1/g was purchased from the Sigma Chemical Co. and used as supplied. 1,2-Dibromodecane (DBD) was prepared by bromination of 1-decene and purified by distillation, followed by passage through an alumina column. All reactions were run in 40 mL centrifuge tubes unless otherwise specified. Shaking refers to agitation on a Burrell Model 75 Wrist Action Shaker.

General Procedure for Lithiation of Polystyrene using TMEDA and n-Butyl Lithium. A modification of the procedure of Grubbs and Su<sup>3</sup> was used. The following is representative: 0.5003 g of polystyrene was flushed with nitrogen, 10 mL pentane added, 0.5 mL (3.31 mM) TMEDA and 1.0 mL (1.6 mM) n-butyl lithium added and the reaction allowed to shake for the desired length of time.

General Procedure for the Lithiation of Polystyryl Bromide with n-Butyl Lithium. A modification of the procedure of Crosby et. al. 4 was used. The following is representative: a flame dried 250 mL round bottomed flask was charged with 2.06 g (8.45 mM Br) 4.1 mM Br/g PSBr, flushed with nitrogen, 100 mL THF added, cooled to -78°C, 6.4 mL (10.24 mM) 1.6 N n-butyl lithium added and the reaction allowed to shake at -78°C.

General Procedure for the Lithiation of Polystyryl Mercuric Chloride. A modification of the procedure of Burlitch and Winterton was used. The following is representative: 0.5024 g (1.41 mM Hg) PSHqCl in 10 mL THF and (6.67 mM) 6.67 N n-butyl lithium, were allowed to shake at -78°C for 1 h and washed with THF to remove excess soluble lithium reagent and dibutyl mercury.

General Analytical Procedure. A suspension of metalated polymer containing ca. 30% or more ethereal solvent at -78°C was allowed to react with 1,2-dibromodecane added slowly at -78°C using a syringe. The resulting polymer suspension was allowed to sit at -78°C for 30 min with occasional shaking and then warmed to room temperature with continuous agitation on a shaker. Aliquouts were withdrawn by syringe, quenched with 10% hydrochloric acid, and the organic solution was used for gas chromatographic analyses.

<u>Preparation of Polystyryl Anthracene</u>. Following the procedure given above, 10.0 g (41.0 mM Br) of 4.1 mM Br/g PSBr was lithiated at  $-78^{\circ}\text{C}$  in 100 mL THF using 38.0 mL (60.8 mM) of 1.6 N n-butyl lithium for 4h. The solvent was removed via cannula, the polymer washed with 50 mL THF, 8.75 g (45.1 mM) anthrone dissolved in 150 mL THF added and allowed to shake overnight. The polymer was filtered, washed with acetone, dried, placed in 200 mL of toluene containing p-toluenesulfonic acid, and refluxed overnight using a Dean-Stark trap to effect the desired dehydration. The polymer was filtered, washed 3 times with 50 mL acetone and dried.

General Procedure for Preparation of Polystyryl Anthracene Radical Anion. Polystyryl Anthracene in THF is treated with the appropriate amount of sodium naphthalene in THF and allowed to shake until all color is transferred to the polymer.

#### References

- Y. Chauvin, D. Commereuc and F. Dawans, <u>Prog. in Poly. Sci.</u>, 5, 95(1977); C.E. Carraher, J. Sheats and C.U. Pittman, Ed., "Organometallic Polymers", Academic Press, New York, N.Y., 1978.
- D.E. Bergbreiter and J.M. Killough, <u>J. Am. Chem. Soc.</u>, 100, 2126(1978).
- 3. R.H. Grubbs and S.H. Su, <u>J. Organometal Chem.</u>, 122, 151 (1976).
- 4. N.M. Weinshenker, G.A. Crosby and J.Y. Wong, <u>J. Org. Chem.</u> 40, 1966(1975).
- 5. J.M. Burlitch and R.C. Winterton, <u>J. Am. Chem. Soc.</u>, 28, 5605(1976).
- 6. H. Gilman and F.K. Cartledge, J. Organometal.Chem., 2, 447(1964).
- 7. S. Mazur and P. Jayalekshmy, <u>J. Am. Chem. Soc.</u>, 101, 667(1979).
- 8. J.I. Crowley and H. Rapoport, <u>Acc. Chem. Res.</u>, 2, 135 (1976).
- G.E. Coates, M.L.H. Green and K. Wade, "Organometallic Compounds, Vol. I, The Main Group Elements", 3rd Ed., Methuen, London, 1969, p. 64; E. Lindner, H. Behrens and S. Birkel, J. Organometal-Chem., 15, 165(1968).
- 10. J.F. Garst, Acc. Chem. Res., 4, 400(1971)...
- H.C. Brown, "Organic Syntheses Via Boranes," Wiley, New York, N.Y., 1975.
- 12. S.C. Watson and J.F. Eastham, <u>J. Organometal Chem.</u>, 9, 165(1967).

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